Growth and Characterization of Co and Ni doped MnO_2 Thin Films for Supercapacitor Applications

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Format for submission of Ph.D. Synopsis /Work plan

Abstract of proposed work plan / Problem:

"Growth and Characterization of Co and Ni doped MnO_2 thin films for Supercapacitor Applications."

In this research work; Co and Ni doped MnO_2 thin films will be deposited onto amorphous and conducting glass substrates by simple chemical deposition Technique. Structural, morphological, optical, electrical and electrochemical properties of the as deposited MnO_2 thin films and Co and Ni doped MnO_2 thin films will be studied by using XRD, SEM, EDAX, UV spectrophotometer, DC electrical conductivity measurement, cyclic voltammetry and galvanostatic charge/discharge measurements.

1. Introduction:-

Thin films are used in a variety of applications due to their unique properties and advantages, and one such application is in the realm of supercapacitors. Supercapacitors, also known as ultracapacitors or electrochemical capacitors, are energy storage devices that bridge the gap between traditional capacitors and batteries. They store and release energy quickly, making them ideal for applications that require rapid energy bursts and high power densities [1-2].

Thin films can be used as electrode materials in supercapacitors. Electrodes are essential components that store electrical energy in supercapacitors. By using thin films, it's possible to increase the surface area of the electrodes, allowing for greater energy storage capacity. Thin films can be engineered to have a high surface area-to-volume ratio, which is crucial for maximizing the energy storage capacity of supercapacitors. The larger the surface area, the more charge can be stored at the electrode-electrolyte interface. Thin films can be made from various nanomaterials such as grapheme, carbon nanotubes, and transition metal oxides. These nanomaterials possess exceptional electrical conductivity and can store a significant amount of charge due to their unique properties at the nanoscale [3-6].

Metal oxides are considered to be promising materials for electrochemical supercapacitors (ES). Among various metal oxide materials reported so far ruthenium oxide (RuO_2)is a major candidate for ES with a moderate value of specific capacitance (SC, 720 F/g) [7]. However, its high-cost and toxicity has made it difficult to find a commercial potential. Hence, alter- native inorganic electrode materials including manganese oxide [8], cobalt oxide [9], copper oxide [10], nickel oxide [11] vanadium oxide [12], tungsten oxide [13], iron oxide [14] etc., have intensively been investigated, owing to their readily availability, chemically stableness, mechanically robustness, safe, environmental friendlineness, and remarkably high performances in SC application [15–17].

To the best of our knowledge, for electrochemical supercapacitor applications few reports have been focused on Co and Ni doped MnO_2 thin films using a cost effective chemical technique.

2. Review of Literature and Development in the subject

A literature review on manganese dioxide (MnO_2) supercapacitors reveals the significant research and development efforts focused on this material for energy storage applications. Manganese dioxide has gained attention due to its high theoretical specific capacitance, low cost, abundance, and environmental friendliness.

Suh Cem Pang et. al. [18] have documented the fabrication of manganese dioxide (MnO_2) thin-film electrochemical capacitor (EC) prototypes with dual-planar electrode configuration. These EC prototypes exhibited good capacitive behaviors in mild Na_2SO_4 aqueous electrolyte. Enhanced capacitive behaviors of EC prototypes were observed upon prolonged voltammetric cycling which could be associated with microstructural transformation of MnO_2 thin-film electrodes from densely packed plate-like to irregular petal-like surface morphology. Effects of voltammetric scan rates, prolonged voltammetric cycling, electrolyte composition, and electrolyte concentration on the surface morphology of MnO_2 thin-film electrodes, and associated capacitive behaviors of MnO_2 thin-film EC prototypes were investigated by cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), and

galvanostatic charge/discharge (GCD) techniques. Results of both CV and EIS indicated that thin-film MnO_2 EC prototypes exhibited the highest specific capacitance of 327 F/g in 0.2 M Na_2SO_4 aqueous electrolyte.

Mai Thanh Tung et. al. [19] synthesized Co and Fe doped manganese oxide thin films were prepared by anodic deposition at current density of 50 mA cm^2 using the electrolyte containing manganese sulfate and either cobalt sulfate or ferrous sulfate. Supercapacitive behavior of Co and Fe doped manganese oxide films were characterized by cyclic voltammetry (CV) and impedance spectroscopy (EIS). The results showed that the doped manganese oxides are composed of nano fiber-like structure with radius of 5-20 nm and remain amorphous structure after heat treatment at 100 degrees C for 2 hours. The average valence of manganese increased from +3.808 to +3.867 after doping Co and from +3.808 to +3.846 after doping Fe. The doped manganese oxide film electrodes exhibited preferably ideal pseudo-capacitive behavior. The specific capacitance value of deposited manganese oxide reached a maximum of 175.3 F/g for doping Co and 244.6 F/g for doping Fe. The thin films retained about 84% of the initial capacity even after 500 cycles of charge-discharge test. Doping Co and Fe decreased diffusion and charge transfer resistance of the films. The electric double layer capacitance and capacitor response frequency were increased after doping.

Pragati A. Shinde et. al. [20] prepared α-MnO_2, β-MnO_2 and Mn_3O_4 nanostructures using simple and convenient hydrothermal method. The impact of three different oxidizing agents, on the structural, morphological and electrochemical performance of prepared nanostructured thin films is investigated. The Mn3O4 nanosheets prepared using potassium nitrate as oxidizing agent exhibits excellent electrochemical features such as, high specific capacitance of 1063 F g^{-1} and high energy density of 94.56 Wh kg^{-1} at current density of 1 mA cm^{-2} along with better cycling stability (95% over 1000 of CV cycles).

Ganesh Sainadh Gudavalli et. al. [21] fabricated arrays of manganese dioxide (MnO_2), a pseudo capacitive material, have been deposited on the carbon fibers (CF) of a carbon woven fabric by Electrodeposition from a solution containing manganese sulfate and sulfuric acid using galvanostatic square waves. The

thickness of the MnO_2 was varied by increasing/decreasing the time of deposition, and the electrochemical performance of the MnO_2 has been analyzed. The CF serves as a substrate material with high surface area, good electrical conductivity and excellent mechanical strength. From the specific capacitance calculations obtained from CV and charge–discharge, a high specific capacitance of 769 F g^{-1} @ 5 mV s−1 (low weight electrode) has been achieved. The maximum area capacitance, estimated from the charge–discharge curves, was 790 mF cm^{-2} @ 5 mV s^{-1}. The high-performance is attributed to the double layer capacitance of the CFs combined with the pseudo capacitive nature of MnO_2, the large surface area, and high degree of ordering of the ultrathin MnO_2.

Jadhav, P. R. et. al. [22] were prepared the amorphous MnO_2 thin films by simple and inexpensive successive ionic layer adsorption and reaction (SILAR) method. The prepared thin films were characterized by means of X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR) and scanning electron microscopy (SEM). The electrochemical study was carried out by cyclic voltammetry in 1 M Na_2SO_4 electrolyte. The films showed the maximum specific capacitance of 243 $F.g^{-1}$ at the scan rate of 10 $mV.s^{-1}$. It is observed that two distinct peaks occurs in cyclic voltammogram during charging and discharging which correspond to the electrochemical oxidation and reduction reaction and different oxidation states of the Mn as Mn^{2+} and $Mn^{3+.}$ Further, the increase in specific capacitance is observed with the increase in the precursor concentration.

Priti N.Jadhav et. al. [23] fabricated tje Manganese Dioxide (MnO_2) Thin-Film prepared by Electrodeposition technique on stainless steel (AISI304) substrate. they studied the effect of thickness on the electrochemical properties of the samples between 600 Sec, 750 Sec, 1050 Sec, and 1200 sec. Best performance for supercapacitor applications was obtained after annealing at 150 °C with a specific capacitance of 136 F g^{-1} at 10mV s^{-1} at 1200 sec. Surface morphology was characterized using Scanning Electron microscope (SEM) for 600 Sec, 750 Sec, 1050 Sec, and 1200 sec. The electrochemical characterization was studied with the help of Cyclic Voltammogram from which maximum value of specific capacitance was estimated to be $136Fg^{-1}$.

3. Objectives of Research/Proposed Hypothesis

Following are the objectives of our research work

1. To deposit good quality MnO_2 thin films and Co and Ni doped MnO_2 thin films by chemical route.
2. To study various properties such as thickness, optical, electrical properties of as deposited samples.
3. To study micro-structural and morphological features of as grown Co and Ni doped MnO_2 thin films.
4. To use these films in supercapacitor applications and study their electrochemical characteristics.
5. To study the effect of technical parameter on Supercapacitive performance of optimum samples of Co and Ni doped MnO_2.

4. Methodology to be adopted:

The chemical method will be used to synthesize the MnO_2 thin films and Co and Ni doped MnO_2 thin films. Unlike the physical methods of preparation of thin films involving evaporation or ejection of material from a source, chemical methods of thin film deposition entail a definite chemical reaction. The chemical method is presently attracting considerable attention as it does not require sophisticated instrumentation like vacuum system and other expensive equipments. The starting chemicals are commonly available and cheap. The preparative parameters are easily controllable and better orientations and improved grain structure can be obtained.

In our present work, Co and Ni doped MnO_2 thin films will be prepared by a chemical method. The deposited thin films will be characterized to study the structural, morphological, optical and electrical properties by means of XRD, SEM, UV-Vis spectrophotometer/FTIR respectively. The Supercapacitive properties of Co and Ni doped MnO_2 thin films will be studied.

Preparation of good quality MnO_2 thin films and Co and Ni doped MnO2 thin films

It is proposed to synthesize Co and Ni doped MnO_2 thin films by chemical method (chemical bath deposition / spray Pyrolysis). Initially the good Co and Ni doped MnO_2 thin films will be deposited on glass and conducting glass substrates. The various preparative parameters like concentration of the ingredients, deposition temperature, thickness and other parameters will be optimized to get good quality Co and Ni doped MnO_2 thin films. They as deposited thin films will be characterized by various characterization techniques in the following manner.

[A] Structural Analysis:

An X-ray diffraction technique will be employed to know the structural changes as a result of Co and Ni incorporation into MnO_2. The interplanar distance (d), intensities of reflections, lattice constants and crystal dimension will be examined and their dependence on composition will be studied.

[B] Compositional Analysis:

The compositional analysis will be done by means of an EDAX or EDS technique and correlation will be made with as taken and observed contents of Co and Ni doped MnO_2 thin films.

[C] Microscopic Studies:

To study the surface morphological features SEM/TEM/AFM technique will be utilized. The crystallographic and morphological information will be used to explain the transport mechanism and optical properties.

[D] Optical Properties:

The optical constants viz optical absorption coefficient (α), the energy band gap (Eg) and mode of optical transition will be determined from optical studies. For this purpose optical absorption / transmission / reflection spectra of the as deposited Co and Ni doped MnO_2 thin films will be studied.

[E] Electrical properties:

The electrical conductivity and thermo-electric power will be measured of all these as deposited thin films. Various terms like carrier concentration (n),

mobility (μ), activation energy (Ea) and barrier height (ϕB) will be determined.

[F] Electrochemical characterization:

Electrochemical capacitors (i.e. supercapacitors) include electrochemical double-layer capacitors that depend on the charge storage of ion adsorption and pseudo-capacitors that are based on charge storage involving fast surface redox reactions. The energy storage capacities of supercapacitors are several orders of magnitude higher than those of conventional dielectric capacitors, but are much lower than those of secondary batteries. They typically have high power density, long cyclic stability and high safety, and thus can be considered as an alternative or complement to rechargeable batteries in applications that require high power delivery or fast energy harvesting. The following electrochemical characterization will be undertaken

1. Cyclic voltammetry
2. Galvanostatic charge discharge studies
3. Electrochemical impedance spectroscopy

5. Importance of study / Society applications:

Thin film based supercapacitors exhibited superior values compared to their bulk and composites of electrodes. Manganese dioxide (MnO_2) supercapacitors, also known as electrochemical capacitors, play a significant role in energy storage and various applications due to their unique properties and advantages.

Supercapacitors, including MnO_2-based ones, have a very high power density compared to traditional batteries. This means they can deliver and absorb energy rapidly, making them suitable for applications requiring quick bursts of power, such as regenerative braking in vehicles and smoothing out fluctuations in renewable energy systems. MnO_2 supercapacitors typically have a longer cycle life compared to conventional batteries. They can endure hundreds of thousands to millions of charge -discharge cycles without significant degradation. This durability makes them suitable for applications where longevity is important, such as in energy storage for grid stabilization or backup power systems.

MnO_2 supercapacitors generally exhibit good performance across a wide

temperature range. Unlike some battery chemistries that can struggle with performance in extreme temperatures, supercapacitors can maintain their effectiveness in both hot and cold environments. MnO_2 supercapacitors are relatively safe compared to some battery types because they don't involve volatile chemicals or flammable materials. This makes them a suitable choice for applications where safety is a primary concern, such as medical devices and aerospace systems.

Supercapacitors are considered more environmentally friendly than some battery technologies due to their longer lifespan and fewer hazardous materials. The longer life reduces the need for frequent replacements, reducing overall waste.

6. Proposed work Plan / Formulation and Structure of Study:

Year-wise plan of work and targets to be achieved

Year I-Plan:

In the first year of the research literature survey and data collection will be done in order to get more information about work already done and scope of the present work. The literature survey includes collection of Journals, books, and related research papers. The chemicals of high purity will be purchased and efforts will be made to deposit good quality Co and Ni doped MnO_2 thin films. At the end of the year two progress reports will be submitted.

Year II-Plan:

In second year, all preparative parameters will be optimized in order to get good quality thin films of Co and Ni doped MnO_2 on conducting glass substrates. The as deposited films will be characterized by various characterizing techniques such as X -ray diffraction (XRD), Scanning Electron Microscopy (SEM), Energy Dispersive Analysis by X-ray (EDAX), UV-Vis photo spectrometer/FTIR and Supercapacitive study. The results will be analyzed and efforts will be made to publish two or more research papers in reputed research journals. Two progress reports will be

submitted at the end of this year.

Year III-Plan:

In the last year, an optimum composition yielding better result will be searched out and effect of technical parameter such as material thickness / heat treatment / impurity concentration will be studied. The results obtained will be analyzed and an attempt will be made to publish it in the reputed journals. Also efforts will be made to share results in the national and international Seminars, Conferences and Workshops etc. during this year. At the end of the year other progress reports will be submitted.

References:

[1] C. Shao, H. Guan, Y. Liu, X. Li, X. Yang, J. Solid State Chem. 177 (2004) 2628.

[2] Z. Chen, J. Lai, C. Shek, J. Non-Cryst. Solids 352 (2006) 3285.

[3] Y.C. Zhang, T. Qiao, X.Y. Hu, J. Solid State Chem. 177 (2004) 4093.

[4] E. Finocchio, G. Busca, Catal. Today 70 (2001) 213.

[5] M. Anilkumar, V. Ravi, Mater. Res. Bull. 40 (2005) 605.

[6] C.B. Berthelin, D. Stuerga, J. Mater. Sci. 40 (2005) 253.

[7] C. Zhao, B. Huang, W. Fu, J. Chen, J. Zhou, E. Xie, Electrochim. Acta 178 (2015) 555– 563.

[8] Y. Asano, K. Nakaoka, K. Murashiro, T. Komatsu, K. Hoshino, Mater. Lett. 81 (2012) 162–164.

[9] S.T. Navale, V.V. Mali, S.A. Pawar, R.S. Mane, M. Naushad, F.J. Stadler, V.B. Patil, R. Soc. Chem. Adv. 5 (2015) 51961–51965.

[10] H. Wu, K. Lian, J. Power Sour. 271 (2014) 534–537.

[11] J. Xu, T. Ding, J. Wang, J. Zhang, S. Wang, C. Chen, Y. Fang, Z. Wu, K. Huo, J. Dai, Electrochim. Acta 174(2015) 728–734.

[12] B.J. Lokhande, R.C. Ambare, S.R. Bharadwaj, Measurement 47 (2014) 427–432.

[13] X. Xia, Y. Zhang, D. Chao, C. Guan, Y. Zhang, L. Li, X. Ge, I.M. Bacho, J. Tu, J.F.Hong, Nano Scale 6 (2014) 5008–5048

[14] D. Choi, G.E. Blomgren, P.N. Kumata, Adv. Mater. 18(2006) 1178–1182.

[15] S.F. Shaikh, J.Y. Lim, R.S. Mane, M.K. Zate, S.H. Han, O.S. Joo, J. Appl. Polym. Sci. 128 (2013) 3660–3664.

[16] A. Kumar, V.K. Raman, Appl. Catal. 138 (2013) 43–50.

[17] F. Fusalba, H.A. Ho, L. Breau, D. Belanger, Chem. Mater. 12 (2000) 2581–2589.

[18] Suh Cem Pang,Boon Hong Wee, Suk Fun Chin, International Journal of Electrochemistry/2011/ Article ID 397685 | https://doi.org/10.4061/2011/397685.

[19] Mai Thanh Tung, Hoang Thi Bich Thuy, Le Thi Thu Hang, J Nanosci Nanotechnol . 2015 Sep;15(9):6949-56. doi: 10.1166/jnn.2015.10525.

[20] Pragati A. Shinde, Vaibhav C. Lokhande, Amar M. Patil, Anuja A. Yadav, Chandrakant D. Lokhande, International Journal of Engineering Research and Technology, Volume 10, Number 1 (2017) 532-537.

[21] Ganesh Sainadh Gudavalli1, James N Turne, Tara P Dhakal, Nanotechnology, Volume 30, Number 45, (2019), 120-126.

[22] Jadhav, P. R. ; Shinde, V. V. ; Navathe, G. J. ; Karanjkar, M. M. ; Patil, P. S. AIP Conference Proceedings, Volume 1536. AIP Conference Proceedings, Volume 1536, Issue 1, p.679-680.

[23] Priti N.Jadhav, Dr. K V Sukhatankar, Dr.B.B.Dhale, National e-Conference on Advanced Materials and Applications, Volume 9 - Issue 7 - Published :23 October 2021 Page No : 74-83.

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